

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
8 April 2004 (08.04.2004)

PCT

(10) International Publication Number
WO 2004/030115 A1

(51) International Patent Classification⁷: **H01L 51/20,**
H05B 33/04

[GB/GB]; Flat 2F2, 92 Montpelier Park, Edinburgh EH10
4NG (GB).

(21) International Application Number:
PCT/GB2003/004247

(74) Agent: **HANSON, William, Bennett;** JY & GW John-
son, Kingsbourne House, 229-231 High Holborn, London
WC1V 7DP (GB).

(22) International Filing Date:
30 September 2003 (30.09.2003)

(81) Designated States (*national*): JP, US.

(25) Filing Language: English

(84) Designated States (*regional*): European patent (AT, BE,
BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU,
IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR).

(26) Publication Language: English

(30) Priority Data:
0222649.6 30 September 2002 (30.09.2002) GB

Published:

- with international search report
- before the expiration of the time limit for amending the
claims and to be republished in the event of receipt of
amendments

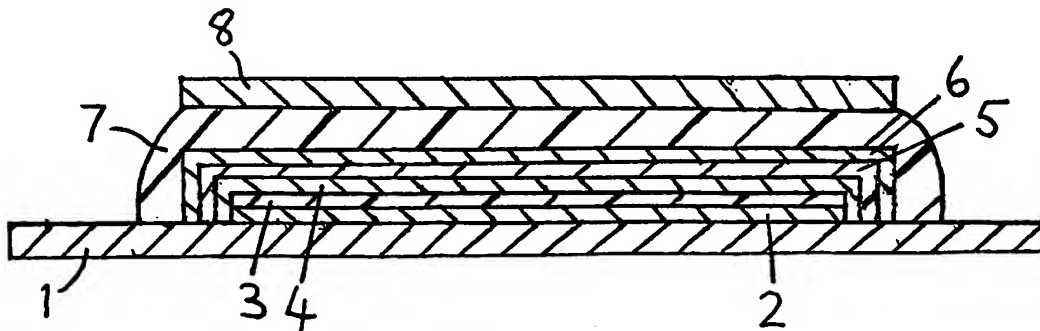
(71) Applicant (*for all designated States except US*): **MI-
CROEMISSIVE DISPLAYS LIMITED** [GB/GB];
Scottish Microelectronics Centre, The King's Buildings,
West Mains Road, Edinburgh EH9 3JF (GB).

(72) Inventor; and

(75) Inventor/Applicant (*for US only*): **BUCKLEY, Alastair**

*For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.*

(54) Title: PASSIVATION LAYER



(57) Abstract: An organic light emitting diode device comprises a substrate (1), a layer (3) of organic, preferably polymeric, light emitting material, and a transparent cathode (4) comprising a layer of material with a work function less than 4 eV. The device has a passivation layer (5) comprising boron oxide.

22 MAR 2005

PASSIVATION LAYER

Background to the Invention

The present invention relates to an organic light emitting diode (OLED) device, a
5 method of manufacturing an OLED device and a passivation layer for an electronic device.

In particular, the OLED may be a polymer light emitting diode (PLED). PLEDs are
usually fabricated on a conductive substrate such as of indium tin oxide (ITO) forming
10 a transparent anode on to which layers of transparent conducting polymer, light emitting polymer, and cathode layers are deposited. A metal can, containing a getter to remove any water and oxygen, is glued over the device to encapsulate it.

Such a "bottom-emitting" device is expensive and slow to manufacture and is bulky.
15

Accordingly, "top-emitting" devices are also known, in which the substrate is opaque, for example a silicon wafer comprising active circuitry. In such devices, the light is emitted through the cathode, which must have very good electrical conductivity and transparency. Advantageously the cathode comprises a layer of calcium, e.g. from 5
20 to 30 nm in thickness.

A major problem with such a device is that both the calcium and the light-emitting polymer are very reactive with oxygen and water. It is therefore known to deposit an encapsulating layer on to the layer of calcium to prevent the ingress of oxygen and
25 water. A large number of possible materials for the encapsulating layer have been suggested. For example, US-A1-20010052752 suggests the use of a dielectric oxide selected from the group consisting of Al_2O_3 , SiO_2 , TiO_2 , ZrO_2 , MgO , HfO_2 , Ta_2O_5 , aluminum titanium oxide and tantalum hafnium oxide. Nitrides, such as silicon nitride, have also been proposed.

30

A serious disadvantage of all of these known materials is that the technique by which they are deposited tends to damage the calcium and/or the light emitting polymer. If

the encapsulation material is deposited by electron beam evaporation, secondary electrons oxidize the light-emitting polymer. If the deposition method is sputtering, both secondary electron ionization and heavy ion damage tend to occur. If plasma enhanced chemical vapor deposition is used, radiofrequency electric fields permeate through the device and permanently degrade its performance. US-A1-20010052752 therefore teaches the use of atomic layer epitaxy as the deposition method, but this is an expensive technique.

It is known to deposit a passivation layer to protect the calcium and light emitting polymer layers from the subsequent deposition of the encapsulating layer. For example, US-A-5739545 describes zinc sulfide as a passivation material. However, the use of zinc sulfide has been found to reduce device lifetime by a factor of 10, possibly because the light-emitting polymer becomes contaminated with sulfur.

15 Summary of the Invention

It is an aim of the present invention to provide a practical and effective passivation layer in a top-emitting OLED.

Accordingly, the present invention provides an organic light emitting diode device having a passivation layer comprising boron oxide.

We have found that when deposited in a film of suitable thickness, boron oxide (B_2O_3) is effective in protecting the device from subsequent deposition techniques such as electron beam deposition and sputtering. Importantly, boron oxide can be thermally deposited. Thermal deposition does not cause damage to the sensitive light emitting polymer or calcium layers. Boron oxide also has a very low coefficient of thermal expansion (about 1 ppm/ $^{\circ}C$ at room temperature) so that the deposited film does not crack. This is unusual, since most inorganic salts that can be thermally deposited crack visibly on cooling. Boron oxide appears to have very few pinholes. Boron oxide films appear to be glassy and amorphous when thermally deposited, unlike most thermally deposited films, which are crystalline.

Preferably, the thickness of the passivation layer is from 50 nm to 1 μ m, and the thickness can be adapted to the energy of the electrons, ions or fields from which protection is required.

- 5 Preferably, the device comprises a substrate, a layer of organic, preferably polymeric, light emitting material, and a transparent cathode comprising a layer of material with a work function less than 4 eV, e.g. calcium. Said passivation layer preferably overlies the layer of material with a work function less than 4 eV directly.
- 10 Preferably, the device comprises an encapsulating layer overlying said passivation layer. The encapsulating layer may comprise any suitable encapsulating material, for example a dielectric oxide selected from the group consisting of Al_2O_3 , SiO_2 , TiO_2 , ZrO_2 , MgO , HfO_2 , Ta_2O_5 , aluminum titanium oxide and tantalum hafnium oxide.
- 15 In a preferred embodiment, the device comprises sealing layers, such as of epoxy resin and glass.

The invention also provides a method of manufacturing an organic light emitting diode device comprising depositing a passivation layer comprising boron oxide on the
20 device.

Preferably, said passivation layer is deposited by thermal evaporation.

- 25 Preferably, the device comprises a substrate, a layer of organic, preferably polymeric, light emitting material, and a transparent cathode comprising a layer of material with a work function less than 4 eV, e.g. calcium. Said passivation layer is preferably deposited directly on to the layer of material with a work function less than 4 eV.

- 30 In a preferred embodiment, the method comprises a further step of depositing an encapsulation layer on to the passivation layer. The encapsulation layer may comprise any suitable encapsulating material, for example a dielectric oxide selected from the group consisting of Al_2O_3 , SiO_2 , TiO_2 , ZrO_2 , MgO , HfO_2 , Ta_2O_5 , aluminum titanium

oxide and tantalum hafnium oxide. Preferably, the encapsulation layer is deposited by electron beam evaporation, but it may alternatively be deposited by sputtering.

5 Preferably, the method comprises sealing the device, for example with epoxy resin and glass.

More generally, the invention provides a passivation layer for an electronic device, the passivation layer comprising boron oxide. As far as we are aware, boron oxide has never been suggested as a passivation material for any application.

10

Brief Description of the Drawings

15 A particular embodiment of the invention will now be described, by way of example only, with reference to the accompanying drawings, in which:

Figure 1 is a schematic cross section of a device according to the invention; and

20 Figure 2 shows the results of an experiment comparing degradation of silicon dioxide and boron oxide.

Detailed Description of the Preferred Embodiment

Figure 1 shows a top-emitting PLED device comprising a silicon substrate 1, a nickel anode 2, a light emitting polymer layer 3 and a transparent calcium cathode layer 4.

25

A passivation layer 5 of boron oxide is deposited on the calcium layer 4 by thermal evaporation. This process comprises simply heating the boron oxide to evaporate it under a suitable vacuum and is the same process used for depositing the calcium layer 4. Boron oxide evaporates at about 1000 °C. The thermal evaporation process does not damage the light emitting polymer layer 3 or the calcium layer 4.

30

The boron oxide layer 5 is "conformal", i.e. continuous without pinholes. This is demonstrated by Figure 2, which shows the results of an experiment comparing silicon dioxide and boron oxide layers. Two test devices 11, 12, each comprised a glass substrate coated with a thin film of calcium. The first device 11 was then coated with a layer of silicon dioxide whilst the second device 12 was coated with a layer of boron oxide. Both devices were submerged in water. In the first device 11, the calcium was degraded at pinholes 13. However, in the second device 12, the degradation was uniform, indicating a conformal film of boron oxide. (Boron oxide is slightly soluble in water and cannot therefore encapsulate on its own.)

10

Returning to Figure 1, an encapsulation layer 6 is deposited by electron beam evaporation on the passivation layer 5. The encapsulation layer is of a suitable encapsulating material such as Al_2O_3 , SiO_2 , Ta_2O_5 or Si_3N_4 .

15 The device is sealed by a layer of epoxy resin 7 deposited on the encapsulation layer 6, also covering the edges of device layers 2 to 6, and contacting the substrate 1. The device is completed by adding a glass plate 8.

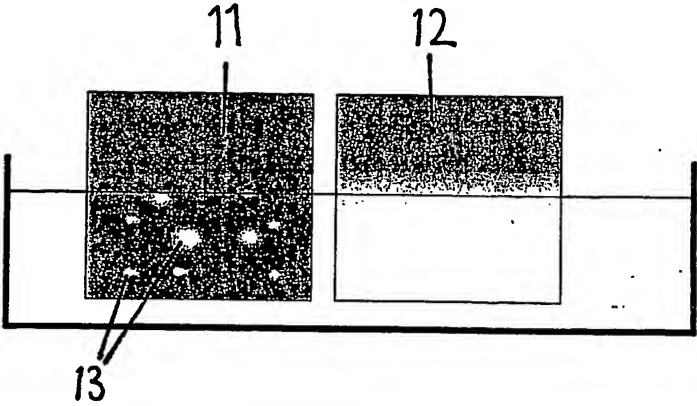
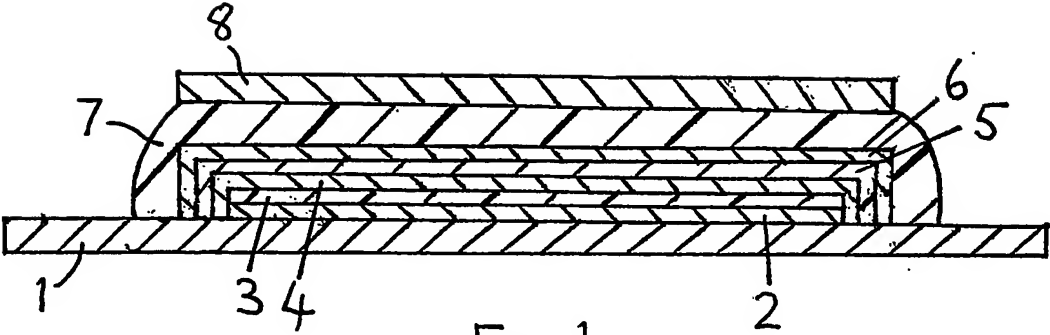
20 All forms of the verb "to comprise" used in this specification have the meaning "to consist of or include".

CLAIMS

1. An organic light emitting diode device having a passivation layer comprising boron oxide.
5
2. A device according to claim 1, comprising a substrate, a layer of organic, preferably polymeric, light emitting material, and a transparent cathode comprising a layer of material with a work function less than 4 eV.
- 10 3. A device according to claim 2, wherein said material with a work function less than 4 eV comprises calcium.
4. A device according to claim 2 or 3, wherein said passivation layer overlies the layer of material with a work function less than 4 eV directly.
15
5. A device according to any preceding claim, comprising an encapsulating layer overlying said passivation layer.
6. A device according to claim 5, wherein the encapsulating layer comprises a
20 dielectric oxide selected from the group consisting of Al_2O_3 , SiO_2 , TiO_2 , ZrO_2 , MgO , HfO_2 , Ta_2O_5 , aluminum titanium oxide and tantalum hafnium oxide.
7. A device according to any preceding claim, comprising sealing layers of adhesive and glass.
25
8. A device according to claim 7, wherein said adhesive comprises epoxy resin.
9. A method of manufacturing an organic light emitting diode device, comprising depositing a passivation layer comprising boron oxide on the device.
30
10. A method according to claim 9, wherein said passivation layer is deposited by thermal evaporation.

11. A method according to claim 9 or 10, wherein the device comprises a substrate, a layer of organic, preferably polymeric, light emitting material, and a transparent cathode comprising a layer of material with a work function less than 4 eV, e.g. calcium.
12. A method according to claim 11, wherein said passivation layer is deposited directly on to the layer of material with a work function less than 4 eV.
13. A method according to claim 9, 10, 11 or 12, comprising a further step of depositing an encapsulation layer on to the passivation layer.
14. A method according to claim 13, wherein the encapsulation layer comprises a dielectric oxide selected from the group consisting of Al_2O_3 , SiO_2 , TiO_2 , ZrO_2 , MgO , HfO_2 , Ta_2O_5 , aluminum titanium oxide and tantalum hafnium oxide.
15. A method according to claim 13 or 14, wherein the encapsulation layer is deposited by electron beam evaporation.
16. A method according to claim 13 or 14, wherein the encapsulation layer is deposited by sputtering.
17. A method according to any one of claims 9 to 16, comprising sealing the device, for example with epoxy resin and glass.
18. A method according to any one of claims 9 to 17, comprising adapting the thickness of the passivation layer to the energy of electrons, ions or fields from which protection is required.
19. A passivation layer for an electronic device, the passivation layer comprising boron oxide.

1/1



INTERNATIONAL SEARCH REPORT

In **national Application No**
PCT/GB 03/04247

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 H01L51/20 H05B33/04		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 7 H01L H05B		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the International search (name of data base and, where practical, search terms used) EPO-Internal		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 1 199 909 A9 (IDEMITSU KOSAN CO) 24 April 2002 (2002-04-24) paragraph '0145! - paragraph '0146!	1-3,5-7, 9-11,13, 14,19
X	EP 1 229 063 A (SUMITOMO CHEMICAL CO) 7 August 2002 (2002-08-07) paragraph '0119! - paragraph '0122!	1-3,5-7, 9,11,13, 14,17,19
X	EP 1 176 850 A (IDEMITSU KOSAN CO) 30 January 2002 (2002-01-30) paragraph '0116!	1,2,5, 7-9,11, 13,17,19
X	US 2001/041268 A1 (ARAI MICHIO ET AL) 15 November 2001 (2001-11-15) paragraphs '0027!, '0048!, '0050!	1,19
-/-		
<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the International filing date "L" document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family		
Date of the actual completion of the international search 3 February 2004		Date of mailing of the international search report 10/02/2004
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3018		Authorized officer Pusch, C

INTERNATIONAL SEARCH REPORT

Int: 1st Application No
PCT/GB 03/04247

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 290 535 A (CHIKARA HIRAYAMA) 6 December 1966 (1966-12-06) column 1, line 28 -column 2, line 59 -----	19
A	US 6 195 142 B1 (GYOTOKU AKIRA ET AL) 27 February 2001 (2001-02-27) column 7, line 33 - line 65 -----	

INTERNATIONAL SEARCH REPORT

Inventor's Application No
PCT/GB 03/04247

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 1199909 A9	24-04-2002	EP 1199909 A1 CN 1365595 T WO 0172091 A1 US 2002038997 A1	24-04-2002 21-08-2002 27-09-2001 04-04-2002
EP 1229063 A	07-08-2002	EP 1229063 A2 JP 2002338665 A US 2002177687 A1	07-08-2002 27-11-2002 28-11-2002
EP 1176850 A	30-01-2002	EP 1176850 A1 CN 1358404 T WO 0158221 A1 US 2001050532 A1	30-01-2002 10-07-2002 09-08-2001 13-12-2001
US 2001041268 A1	15-11-2001	JP 11195487 A	21-07-1999
US 3290535 A	06-12-1966	DE 1273757 B GB 965339 A NL 284885 A	25-07-1968 29-07-1964
US 6195142 B1	27-02-2001	JP 10041067 A JP 10125463 A	13-02-1998 15-05-1998